



Original Article

The exfoliation of irradiated nuclear graphite by treatment with organic solvent: A proposal for its recycling

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ABSTRACT

For the past 50 years, graphite has been widely used as a moderator, reflector and fuel matrix in different kinds of gas-cooled reactors. Resulting in approximately 250,000 metric tons of irradiated graphite waste. One of the most significant long-lived radioisotope from graphite reactors is carbon-14 (¹⁴C) [1] with a half-life of 5730 years, this makes it a huge concern for deep geologic disposal of nuclear graphite (NG). Considering the lifecycle of NG a number of waste management options have been developed, mainly focused on the achievement of the radiological requirements for disposal [2]. The existing approaches for recycling depend on the cost to be economically viable.

In this new study, an affordable process to remove ¹⁴C has been proposed using samples taken from the Nuclear Power Plant in Latina (Italy) which have been used to investigate the capability of organic and inorganic solvents in removing ¹⁴C from exfoliated nuclear graphite, with the aim to design a practicable approach to obtain graphite for recycling or/and safety disposed as L& LLW.

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1. Introduction

Recently the production of graphene by treatment of graphite has increased. Graphene has outstanding optical, electronic and mechanical properties [3] and is used for large-scale applications. Various methods have been proposed to prepare graphene [4] and with regards to this it has been demonstrated that the exfoliation of graphite in a liquid media could be assisted by using a different class of molecules. Due to the emerging interest in the field of carbon nanoscience, the majority of studies on chemistry of graphene involves Highly Oriented Pyrolytic Graphite (HOPG) or Graphene Oxide (GO) but only very few are related to NG. This, coming from nuclear installations, has different characteristics in respect of other kinds of radioactive waste due its physical and chemical properties because of the presence of tritium and ¹⁴C [1]. Over the last twenty years, numerous proposals have been made for the long-term treatment of radioactive graphite wastes [2] but only the process proposed by Fachinger [5] hypothesized a possible method for the graphite recovery. Nowadays, graphite can be exfoliated by different

chemical methods in the liquid phase. One of the simplest approaches to disperse graphene sheets is ultrasonic treatment in organic solvents, which makes graphite's atomic planes chemically loosened and intercalated. Some dipolar aprotic solvents such as N, N-Dimethylacetamide (DMF) or N-Methylpyrrolidone (NMP) have been shown to be effective in the stabilization of graphene in (a) solution without re-aggregation [6,7]. These dispersions have some drawbacks: it has been pointed out that most organic solvents tend to be toxic so it would be preferable to achieve concentrated graphene dispersion in low toxic and low-boiling point solvents. Ricardo [8], reported the effect of basic aqueous mixtures of salts as lithium, potassium and sodium chloride (pH 11) on the exfoliation process and the capability of mixture water/acetone to produce highly stable graphite dispersion [9]. In this study, the reaction of NG towards the exfoliation method process solvent and its effects on the ¹⁴C removal have been studied, with the aim to propose a possible approach to produce graphite for recycling.

2. Materials and methods

2.1. Optimization of experimental parameters

The concentration of ¹⁴C on the surface of graphite blocks is

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dependent on its location within the reactor, core design, flux, manufacturing and environment. Graphite naturally absorbs air; consequently ^{14}N and ^{17}O are readily found on the graphite surface. Oxygen and nitrogen absorption occurs during graphite manufacturing, component assembly and storage as a result of air leaks into the reactor coolant gas. The neutron capture cross sections and isotopic abundances of ^{14}N and ^{17}O (Table 1) indicate the neutron activation of ^{14}N is likely to be the main source of ^{14}C on the surfaces of irradiated graphite neutron absorption. ^{13}C can be also a significant contributor to the total amount of ^{14}C , but this source is homogeneously distributed throughout a graphite component [10].

The carbon chemical forms which can be predicted under the reactor conditions [11] are summarized in Table 2.

Three irradiated NG samples (named iGF1; iGF3; iGF4), have been taken from the Nuclear Power Plant in Latina (LT) Italy. This plant was a GRC Magnox Gas Cooled reactor (CO_2) in operation from 1963 to 1987. The graphite, used as moderator in this plant, has been exposed to a maximum neutron flux of $5 \times 10^{22} \text{ n/cm}^2$. IGF1; iGF3; iGF4 have been crushed, ground and passed through a sieve with a mesh size of 0.5 mm and treated with N,N-Dimethylacetamide (DMF), N-Methyl-2-pyrrolidone (NMP) and N,N-Dimethylformamide (DMF). Aliquots of iGF4 has been treated with a mixture solvents/NaOH pellet (50 mg/ml), and a water/acetone (15/85% v/v).

Since the effect of the solvent base exfoliation on NG has never investigated, the optimization of the experimental parameters was required.

The ratio graphite powder/solvent has been evaluated taking into account that one of the most of the effective methods to reduce the strength between the adjacent layers is liquid immersion. Several tests with five different NG graphite amounts (5–10–25–50–75 mg) were performed. The samples were treated with 5 ml of N-Methyl-2-pyrrolidone (NMP), N,N-Dimethylacetamide (DMA), N,N-Dimethylformamide (DMF) and filtrated on Polyvinylidene Fluoride (PVDF) 0.1 μm . All the solvents are analytical grade. The solutions were sonicated for 3 h in a sonication bath at 30 Watt of power and 37 kHz; then centrifuged at 500 rpm for 90 min. The PVDF filters with the upper dispersed material have been dried in a vacuum oven at 60 °C for 2 h at 100 mbar and weighed in order to obtain the amount of graphitic material. The trend as a function of the ratio of graphite powder (mg) versus solvent (ml) is showed in Fig. 1.

Graphene concentration after centrifugation has been determined experimentally via UV–Vis analyses at 660 nm with an UV–Vis Agilent (mod.CARY 60). As showed in Fig. 2, the optical absorbance, divided by cell length, plotted versus concentration of graphene (mg) in the solvents, has shown a Lambert-Beer behaviour.

Sonication time is another crucial point that would be optimised. When the sonication goes on over 3 h, the bath heats up to $\sim 60^\circ\text{C}$ and evaporation can occur. In order to avoid the degradation of the solvents, the experiments were carried taking under control the bath temperature with a refrigeration device. Since the sonication is a complex process [12]; water level and volume of dispersion of each sample have been carefully measured. The material in the dispersion after sonication is composed of thick graphite like-flakes, as sediment, and small flakes in the

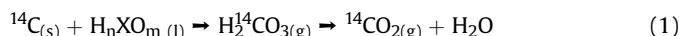
supernatant. The experimental data in Fig. 3 showed that the removal process seems to be effective starting from third hours of sonication: to investigate the trend of the process, the evaluation of the ^{14}C removed has been carried out after 5 and 10 h.

Finally, the selected experimental parameters are illustrated in Table 3.

2.2. ^{14}C concentration in irradiated graphite samples

In the moderator graphite, over 60% of ^{14}C is produced by interaction with nitrogen impurities enclosed in the graphite and 40% by interaction with ^{13}C contained in the graphite pile [3]. For ^{14}C gas phase extraction in iGF samples, a closed system under inert gas flow (N_2) has been mounted as shown in Fig. 4. For each sample, 0.1 g of powder has been added to 100 mL of a mixture of $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--HClO}_4$ 8:3:1 v/v/v. and heated at 200 °C. Wet Oxidation Acid Digestion was carried out under N_2 flow and ^{14}C was trapped as CO_2 in 3-MPA(3-methoxypropylamine), as showed in Fig. 4.

The chemical reaction is described below (Eq. (1)).



$^{14}\text{CO}_2$ obtained was measured by Liquid Scintillation Counting LSC with a LSC HIDEX 300SL TDCR. The results, expressed in Bq/g, are showed in Table 4.

2.3. Exfoliation process and solvent removal efficiency

Aliquots of the iGF1, iGF2 and iGF4 graphite samples have been treated with 5 ml of DMA, NPM, DMF, sonicated for 3,5, and 10 h, centrifuged to remove the thick graphite and filtered on PDFV, to remove the light flakes of graphene. The clarified solution was measured by Liquid Scintillation Counting: the results are showed in Table 5.

Table 6 shows the results obtained on sample iGF4 with a mixture of the same organic solvents with NaOH pellets (50 mg/ml) and with a ternary mixture (water 15%; acetone 85%; NaOH). All the aliquots were exfoliated for 3; 5 and 10 h, following the experimental condition reported in Table 3.

Removal efficiency is defined as the ratio between the activity (Bq) measured in the exfoliated samples and the activity (Bq) in pristine NG. Removed activity from exfoliated sample is defined as the ratio between the measured activity (Bq) in the exfoliated samples and the calculated activity (Bq), depending on the yield of exfoliation, on the same samples.

3. Results and discussion

This paper evaluates the possibility to apply the exfoliation method ultrasound assisted to remove ^{14}C from the nuclear graphite, providing a procedure to reduce the NG toxicity and/or produce graphene from NG recycling. The sonication allows the solvent to easily reach the target radiocarbon in the closed porosity and extract it: successful exfoliation requires the overcoming of the Van der Waals attractions between adjacent layers. It was demonstrated by Hernandez [13] that the most appropriate solvents, as characterised by the fraction of graphite/graphene remaining after centrifugation, have a surface tension (γ) between 25 and $\sim 45 \text{ mJm}^{-2}$. Furthermore it has been described by Liu [14] that NaOH can be added to organic solvent to increase the direct exfoliation of graphene. Since the final purpose of this paper was not only to evaluate if the exfoliation method could be applied to NG, but especially to investigate its potential on the removal of radiocarbon, several experiments with organic solvents and with organic/

Table 1

Properties of ^{14}C precursors available in reactor-irradiated graphite. Reaction cross-section values refers to thermal neutron energy (0.025 eV).

Reaction	Cross Section (barns)	Natural isotopic abundance (%)
$^{14}\text{N}(n,p) ^{14}\text{C}$	1.8	99.63
$^{13}\text{C}(n,\gamma) ^{14}\text{C}$	0.0015	1.07
$^{17}\text{O}(n,\alpha) ^{14}\text{C}$	0.235	0.04

Table 2
Chemical forms of ^{14}C under reactor conditions.

$^{13}\text{C}(n,\gamma)^{14}\text{C}$	$^{14}\text{C} \rightarrow$	In structural lattice
$^{17}\text{O}(n,\alpha)^{14}\text{C}$	$\text{O}_2 \rightarrow$	^{14}CO ; $^{14}\text{CO}_2$
$^{14}\text{N}(n,p)^{14}\text{C}$	$^{14}\text{C}-\text{C} \rightarrow$	CO , CO_2 , HCO_3^- , CO_3^{2-} ; CH_x , $-\text{COH}$, $-\text{CO}-$, $-\text{COOH}$, CH_4 ,

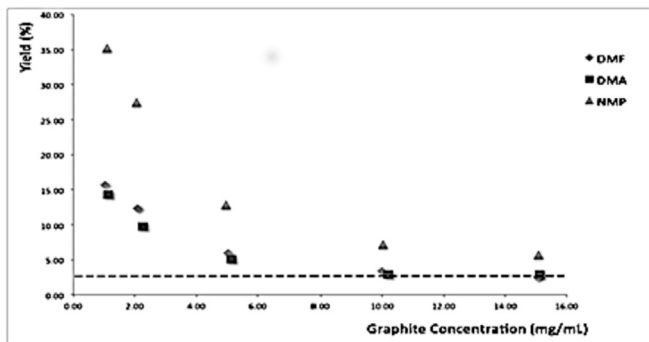


Fig. 1. Optimization of ratio graphite(mg)/solvent (ml).

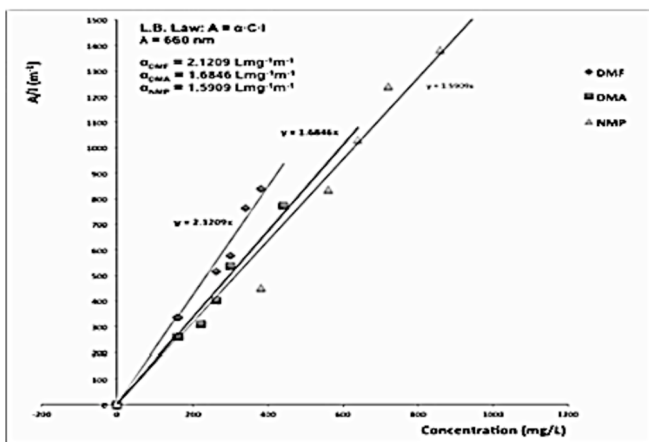


Fig. 2. Absorption coefficient at 660 nm for graphene in NMP, DMA and DMF.

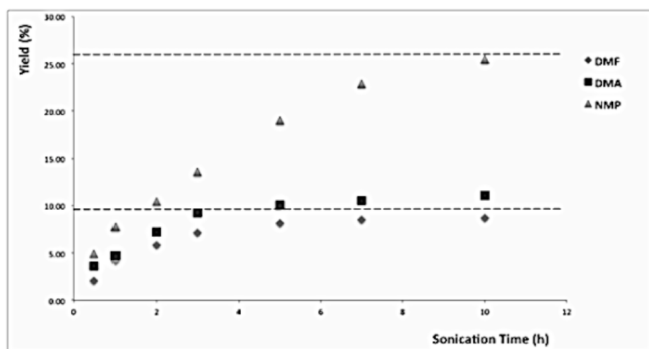


Fig. 3. Effect of the sonication with DMF, DMA and NMP (h).

inorganic mixture have been performed. In Tables 4 and 5 the results obtained are summarized by applying the method: the mixture organic/inorganic solvents shows a better capacity in removing ^{14}C from the exfoliated nuclear graphite producing a complete stable exfoliation. These results are consistent with the evidences obtained by Nonomura [7] that demonstrated the ability

Table 3
Experimental conditions.

Graphite (NG)	10 mg
Solvent (each)	5 ml of DMF, DMA, NMP
Time of sonication	3-,5-,10 h
Sonication Power	30W–37 kHz
Centrifugation	500 rpm for 90 min
Separation	Filtration on PVDF 0.1 μm

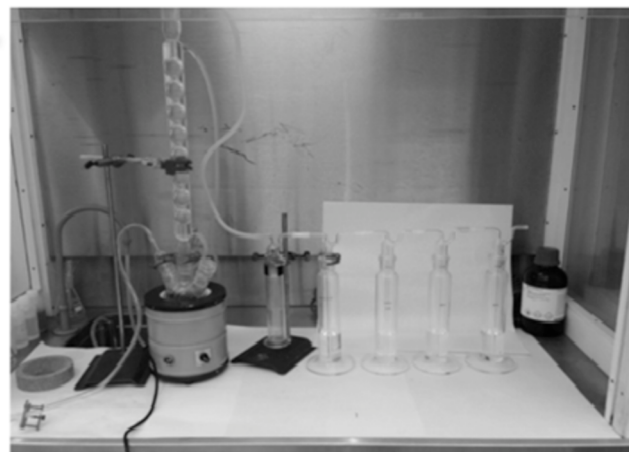


Fig. 4. Determination of ^{14}C by wet oxidation acid digestion of the graphite samples.

Table 4
 ^{14}C characterization on iGF samples.

Sample	^{14}C (Bq g^{-1})
iGF1	8505 (± 10)
iGF3	12886 (± 23)
iGF4	8552 (± 12)

of different aqueous/non aqueous mixtures to produce highly stable dispersions [1]. Under this condition it is credible to assert that NaOH, according to the results showed in Table 6, it is possible to transform ^{14}C in different chemical forms of carbonate (see Table 2) which are easily soluble in water.

4. Conclusion

The decontamination of nuclear graphite has been occasionally faced by some researchers [4,8] using thermal and chemical treatments. With this work we want to demonstrate that is possible to obtain a substantial removal of ^{14}C after achieving a stable graphite particle dispersion from NG samples using a mixture of solvents at alkaline pH value. First the removal efficiency of organic solvents at different polarities have been determined, then the effects on NG of inorganic/organic mixture solvents have been investigated. The achieved results indicate that it essential attain a stable graphite dispersion to allow NaOH to act more effectively.

Ongoing work to optimised this process includes the

Table 5
Removed activity(%) on NG samples exfoliated by DMF, DMA, NMP.

Sample	solvent (5 ml)	time (h)	Removal Efficiency (%)	Removed activity from exfol. sample(%)
iGF1	DMF	3	0.12	1.88
		5	0.45	3.23
		10	0.34	1.21
	DMA	3	0.02	0.84
		5	0.22	2.28
		10	0.41	2.14
	NMP	3	0.09	0.72
		5	0.11	0.41
		10	0.32	0.42
iGF3	DMF	3	0.06	0.84
		5	0.21	1.70
		10	0.29	1.82
	DMA	3	0.10	0.65
		5	0.38	1.66
		10	0.48	0.93
	NMP	3	0.24	1.11
		5	0.20	0.66
		10	0.33	1.01
iGF4	DMF	3	0.16	3.39
		5	0.17	2.72
		10	0.27	1.23
	DMA	3	0.04	1.46
		5	0.06	2.14
		10	0.14	2.42
	NMP	3	0.19	4.04
		5	0.19	1.48
		10	0.44	1.78

Table 6
Removed activity(%) on i-GF4 sample exfoliated by solvent mixture.

Solvent (5 ml)	Time (h)	Removal Efficiency (%)	Removed activity from exfol. sample (%)
DMF/NaOH	3	0.28	5.53
	5	1.26	12.84
	10	1.93	15.04
DMA/NaOH	3	0.17	5.81
	5	1.16	11.09
	10	2.06	17.43
NMP/NaOH	3	1.05	13.97
	5	2.77	17.19
	10	4.15	21.97
Water-Acetone (15–85%)/NaOH	3	14.00	16.61
	5	15.25	17.51
	10	22.76	23.85

investigation of the “Removal efficiency” of some alkaline mixture solvents in order to raise the amount of ^{14}C extracted producing a small volume of contaminated solvent which can be easily reduced and confined.

Declaration of interest

The authors have been approved the final version of the manuscript submitted. There is no financial or personal interest.

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